

## PATENT SPECIFICATION

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(54) CORROSION RESISTANT COATINGS AND PROCESS  
 FOR MAKING THE SAME

(71) We, UNION CARBIDE CORPORATION, a corporation organized and existing under the laws of the State of New York, United States of America, of 270 Park Avenue, New York, State of New York 10017, United States of America, (assignee of ROBERT CLARK TUCKER, JR.), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing a metallurgically sealed coating which effectively protects a substrate from oxidation and/or corrosion attack.

The most common type of corrosive attack of metal alloys, such as nickel and cobalt base superalloys, is, of course, oxidation in air. This problem limits the temperature at which unprotected alloys can be practically used to values lower than those dictated by loss of mechanical strength with increasing temperature. Other types of corrosive attack may also occur which prohibit the use of an alloy within a given temperature range or above a certain temperature. For example, superalloys, particularly those with a nickel base, are subject to what is commonly called "hot corrosion" and "sulfidation" at intermediate temperatures if various salts or sulfur are present in the high temperature environment to which they are exposed. It is well known that the useful life of an alloy at a given temperature, or the upper temperature at which it is useful, can be extended by the application of protective coatings.

There are many excellent coatings available for providing a metal alloy substrate with a surface having specific characteristics suitable for a particular end use application. The coating may be applied to increase the wear-resistant characteristics of the substrate, decrease the contact-friction characteristics of the substrate, electrically or thermally insulate the substrate, or protect it from oxidation or other corrosive attack. Many such coatings, however, are inherently porous, as are the

plasma deposited and detonation gun coatings, and thereby allow liquid or gas mediums in an end use environment to permeate to the substrate where the medium can attack and corrode the substrate. Thus an otherwise perfectly good coating for a particular purpose may be ineffective due to inherent porosity.

The most commonly used coatings for superalloys for corrosion resistant applications are those of the aluminide type which are produced by the diffusion/reaction of aluminum with the surface of the alloy. However, in recent years the service requirements demanded of alloys have increased and as a result complex, multi-element coatings have become popular. Moreover, since the coating is formed by reaction with the substrate, the mechanical strength of the substrate is effectively lowered by the reduction in cross section of the unaltered substrate. This has become a severe problem in thin-section applications such as turbine blades.

Several methods are available for producing complex coatings, but all are expensive and some are limited to binary or ternary coatings. These methods include the successive application of single-element layers of the various components of the coating by electroplating, immersion in molten metal, pack cementation, electrophoresis, or a combination of these methods. Usually these layers are then diffused together by heating the component to an elevated temperature in an inert atmosphere. These techniques are expensive because of the multiple processing steps involved and they are usually limited to coatings of two or three elements applied as single elements. A more sophisticated method, physical vapor deposition, is capable of depositing multiple element coatings in one step, but is extremely expensive because, among other things, it must be done in a high vacuum.

Concerning the inherent porosity of coatings, several methods have been developed for sealing such coatings so as to provide an effective barrier to protect the substrate from attack by corrosive elements. One such

method is to impregnate the coating with a silicone, an epoxy resin or a similar material which is highly resistant to many aqueous corrosive environments. This technique, however, requires a delicate process procedure for infiltrating the sealants into the pores of the coating and in addition, the sealants are unsuited for high temperature, highly corrosive environments, such as molten zinc, molten aluminum, high temperature air and the like, because of decomposition, oxidation and/or melting of the sealants.

Another method for sealing a porous type coating is to impregnate the coating with a low-melting metal which may effectively retard attack in some environments but would be ineffective in high temperature corrosive environments where it would very likely decompose, oxidize and/or melt. It may also react with, and degrade the properties of either the coating or the substrate.

Other methods that have been developed include the flame spraying of two or more selected metals that will react exothermally during spraying to produce an intermetallic compound that will effectively bond to the substrate. These coatings may have less porosity than conventional types of flame sprayed coatings, such as metals, alloys or ceramic coatings, but are not completely sealed.

The present invention overcomes the technical and economical drawbacks of the prior art by being directed to a metallurgically sealed coating produced by the simultaneous plasma deposition of an intimate mixture of at least two materials which are deposited in the unreacted state so that when subjected to a heat treatment in a non-contaminating atmosphere, a reaction/diffusion will occur between the materials. The coating so produced will generally have little or no reaction with the substrate it is protecting, and consequently, the strength of the substrate will not be affected or reduced.

This invention is directed to a process for producing a metallurgically sealed coating. Specifically, the invention relates to a process for producing a coating by simultaneously depositing, by plasma-spraying techniques, a layer of an intimate mixture of two or more materials, each of which is selected from at least one of the groups consisting of metals, alloys, and intermetallics, onto a substrate in a substantially unreacted state, and thereafter subjecting the deposited layer to an elevated temperature in a non-contaminating atmosphere for a time period sufficient to react/diffuse the materials in said layer to produce a metallurgically sealed coating of a substantially homogeneous alloy and/or intermetallic. The coating produced will effectively provide a barrier that will be inert or highly corrosion resistant in high temperature corrosive environments, such as air and other

oxidizing gases at high temperatures. High temperature is intended to mean a temperature above which corrosion of an uncoated substrate material would begin and rapidly continue. This temperature is a function of the medium in the environment and the composition of the substrate, and once both are known, an artisan can readily determine its numerical value.

The coated articles of this invention can also admirably be used in lower temperature environments presenting a severe corrosion problem; however, economics may limit the use of such coated articles under such conditions.

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The metallurgically coated layer of this invention is initially an as-deposited layer, applied by plasma techniques, comprising a mechanical mixture of two or more materials with significantly different chemical activity, such chemical activity being defined beginning on page 91 of the text titled "The Theory of Transformation in Metals and Alloys" by J. W. Christian, Pergamon Press-Oxford, 1965 edition. Thus there exists in the coated layer a driving force, over and above the ordinary driving force of surface free energy that causes conventional sintering. In such an as-deposited coating, this additional energy appears to be necessary to achieve densification and sealing at temperatures and within reasonable time periods. Conventional plasma-deposited coatings usually have a significantly lower coefficient of thermal expansion than the usual metallic substrates and thus when a coated substrate is heated, the coating tends to crack perpendicular to the surface and to shear the bond line with the surface. Moreover, this problem is compounded by the high residual tensile stress frequently present in an as-deposited coating. During the heat treatment of the metallurgical coating of this invention, the shrinkage that occurs due to reaction/diffusion between the materials tends to relieve this residual stress, and on subsequent thermal cycling in end use applications, the coating adheres to the substrate without spalling or shearing along the bond line.

Some examples of substrate materials used in various corrosive environments include, but not limited to, metals and alloys, such as steel, stainless steel, iron base alloys, aluminum, aluminum base alloys, nickel, nickel base alloys, cobalt, cobalt base alloys, copper, 130

copper base alloys, chromium, chromium base alloys, refractory metals, and refractory metal base alloys.

The coating of this invention must be composed of at least two materials, each of which is selected from at least one of the groups consisting of elemental metals, alloys, and intermetallics (compound metals in which the atoms have a distinct spatial arrangement) and such materials must be deposited on the substrate in an unreacted state; e.g., an interlocking lamellar structure composed of splats of the individual materials. The selection of the two or more materials for the coating is important since they must react/diffuse together at an elevated temperature so as to form a substantially homogeneous alloy and/or intermetallic; be compatible with the substrate such that they form a good bond while not significantly interdiffusing with the substrate upon being subjected to a heat treatment or when subjected to a particular end use environment; and after reaction/diffusion has occurred, they must be capable of forming a substantially effective barrier between the substrate and any corrosive type medium that may exist in its intended end use environment. The as-deposited mixture of elements, alloys, or intermetallics will have an inherent interconnected porosity offering a direct access to the substrate for environmental gases. However, during the heat treatment in a non-oxidizing atmosphere, this porosity will, for the most part, be eliminated and any small amount of porosity remaining will consist of closed pores. Thus the reaction/diffusion that occurs during the heat treatment in a non-oxidizing atmosphere will effectively seal the coating and provide a barrier for the substrate by eliminating any direct open paths for corrosive gases between the substrate and the environment. Although a substantially homogeneous alloy or intermetallic may be formed at the elevated temperature during the heat treatment, a precipitation may occur during cooling to ambient temperature whereby the precipitate would be distributed in a solid or alloy matrix, such precipitate being an alloy or intermetallic formed from the deposited materials of the coating. Also, a transient intermetallic may form during the heat treatment which would convert to an alloy upon completion of the heat treatment. Thus at any particular time during the heat treatment, an intermetallic compound and an alloy, both formed from the materials of the coating, may exist simultaneously. However, in the preferred embodiment, a coating composed of a substantially homogeneous alloy or intermetallic would be desirable although a coating composed of an intermetallic compound distributed substantially throughout an alloy matrix would be suitable in certain applications.

The useful life of the coating can be pro-

longed by incorporating into the coated layer discrete particles of metal oxides. The dispersion of metal oxide particles throughout the coated layer is believed to substantially reduce spalling of the protective scale on the coating when used in its intended service environment, and also it is believed that such particles reduce the diffusion rate of some of the elements in the coating. Examples of some metal oxides include such compounds as alumina ( $\text{Al}_2\text{O}_3$ ), silica ( $\text{SiO}_2$ ), chromium sesquioxide ( $\text{Cr}_2\text{O}_3$ ), hafnium oxide ( $\text{HfO}_2$ ), zirconium oxide ( $\text{ZrO}_2$ ), magnesium oxide ( $\text{MgO}$ ), yttrium oxide ( $\text{Y}_2\text{O}_3$ ), rare earth oxides, and titanium dioxide ( $\text{TiO}_2$ ). The metal oxide particles should be sized between about 0.01 micron and about 50 microns, preferably between about 0.1 and about 1 micron, and occupy between about 1% and about 75% by volume of the coating composition, preferably between about 2% and about 55% by volume, to provide the necessary improvement in the useful life of the coating in its intended environment.

The heat treatment and temperature required to achieve substantial homogenization and sealing during the reaction/diffusion step are a function of the materials of the coating. It is essential, however, that during deposition by plasma or detonation gun techniques, a minimum of oxidation of the materials occurs, and that the as-deposited composition consists of a mechanical mixture of discrete, essentially unreacted materials. If these requirements are not substantially met, the interaction between the materials during the reaction/diffusion step will be impeded and complete sealing will not occur. Although interdiffusion between the coating and the substrate should be very small in most cases, a minor amount may tend to increase the bond strength.

The particular materials selected for coating a substrate should, after the reaction/diffusion step, be resistant to the corrosive medium that will exist in the intended end use environment of the coated substrate. In some applications the selected reacted coating material may not possess the corrosion resistant characteristics necessary for a particular end use application and therefore an additional process step may be required for enhancing such characteristics. A conventional oxidizing, carburizing, nitriding, boriding, siliciding or the like, step may be sufficient to develop a corrosion resistant oxide, carbide, nitride, boride, silicide, or the like, respectively, on the top layer of the coating. This process treatment may be carried out in a controlled environment under partial pressure conditions so as to react only one of the materials in the coated layer and thereby control the formation of the layer thickness on the substrate to a height sufficient to protect the substrate against corrosion in its

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intended environment. If the end use or service environment is an oxidizing, nitriding or similar environment, then the particular oxide, nitride or similar compound chosen, respectively, should be a very slowly developing compound; i.e., growth controlled by slow diffusion as occurs in  $Al_2O_3$ .

Suitable materials for use in the coated layer include elemental metals such as nickel, aluminum, cobalt, iron, chromium, copper, molybdenum, tungsten, niobium, silicon, tantalum, titanium, zinc, manganese, zirconium, vanadium, and hafnium, and alloys or intermetallics of the above element metals such as Nichrome (Registered Trade Mark), iron-chromium, cobalt-chromium, nickel-chromium-silicon, cobalt-chromium-silicon, iron-chromium-silicon, iron-chromium alloys containing rare earth additions, nickel-chromium alloys containing rare earth additions, cobalt-chromium alloys containing rare earth additions, and copper-aluminum. For the purpose of this invention, yttrium is included as one of the rare earth metals.

Any artisan can determine the choice of the coated materials that can be deposited in an unreacted state and thereafter upon being subjected to a heat treatment produce a substantially homogeneous alloy and/or intermetallic impervious coating, once the substrate is selected, and the intended end use environment is known.

The total composition of the coating; i.e., the sum of the mixture of elements or alloys, can be so chosen that it not only forms a corrosive resistant coating, but also results in very limited or no interaction with the substrate during heat treatment or service. For example, during the application or heat treatment of a typical aluminide coating on a nickel base superalloy, the compound  $NiAl$  is formed by the diffusion of Ni outward from the substrate. This results in a complex change in the composition of the substrate with the formation of a columnar array of phases perpendicular to the surface and a weakening of the substrate to significant depth. As previously stated, on components with a thin cross section this can lead to a serious degradation of properties. However, this diffusion loss can be avoided by choosing a total coating composition in which the final chemical potential of Ni in the coating is approximately the same as the potential of Ni in the substrate. At the same time the coating composition may include other elements with extremely low diffusion rates which greatly increase the corrosion resistance of the coating, but would have little deleterious effect on the mechanical properties of the substrate. An example of this would be the addition of yttrium or some other rare earth metal, to a complex coating designed for superalloys. The rare earth metal would remain in the coating either because it was

present as a stable intermetallic compound or because its diffusion rate in the matrix is extremely low. Similarly a dispersion of yttria or some other rare earth oxides, which would also enhance the oxidation resistance of Fe, Ni, or Co base alloys, can be achieved very inexpensively in a plasma-deposited coating and would remain positionally stable. The temperature at which the reaction/diffusion occurs between the selected materials of the coating is a function of such materials and can be readily determined from any good metallurgical test reference.

A non-oxidizing atmosphere is required during the heat treatment of this inventive process to prevent a layer, such as an oxide layer, from interfering with the reaction/diffusion step of the process. A suitable non-contaminating atmosphere would be an inert atmosphere such as argon, helium, or vacuum, or a reducing atmosphere such as hydrogen.

When the reacted coated layer is to be oxidized, carburized, nitrided, silicided, borided or the like, to increase its corrosion resistance, then conventional processing techniques can be used. For example, the coating can be oxidized by exposure to a mixture of  $H_2O$  and  $H_2$  in such ratios that only the desired component of the coating is oxidized, such as aluminum in a nickel-chromium-aluminum coating. Nitriding of the top surface of the coating can be accomplished by exposing the coating to nitrogen or ammonia at elevated temperatures. The top surface of the coating could be carburized by exposure to methane at elevated temperatures. Likewise, siliciding or boriding of the top surface of the coating could be accomplished by conventional techniques. The degree of formation of the oxide, nitride, carbide, silicide or boride layer should be sufficient to produce the desired corrosion resistant characteristics necessary for the coating when it is exposed in a particular environment.

In generally many alloys could be protected by the proper choice of a coating composition. Specifically, substrates, composed of Fe, Ni or Co base alloys can be enhanced by the application of coatings of the type Fe-Cr-Al-Y, Ni-Cr-Al-Y, or Co-Cr-Al-Y, respectively. Other suitable coatings include Ni-Cr-Al, Co-Cr-Al, Fe-Cr-Al, Ni-Cr-Si-Al, Co-Cr-Si-Al, and Fe-Cr-Si-Al. In these coatings, the aluminum proportion could vary from between about 8 wt/o and about 25 wt/o the coating composition, the chromium between about 10 wt/o and about 25 wt/o the coating composition with the remainder either nickel, iron or cobalt. When a rare earth element, such as yttrium, is included, its proportion could vary from between about 0.01 wt/o and about 5 wt/o the coating composition.

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tion. Likewise, if silicon is included in the coating composition, it could be present in an amount between about 0.10 wt/o and about 5.0 wt/o the coating composition. To achieve a minimum of interaction, the composition of the coating should be compatible with the substrate; however, superior oxidation resistance may be achieved with some other combination. Another general class of alloys which would be protected by the process of this invention are the refractory metals Cr, Nb, Ta, and Mo for which various silicide coatings have been shown to provide good oxidation resistance, such silicide coatings containing Si and at least one material selected from the group consisting of niobium, tungsten, chromium, titanium, vanadium, aluminum, boron, iron, and manganese. Likewise, it has been found that copper substrates can be protected by an aluminum and copper base alloy composition applied in accordance with this invention.

The first step in the application of this invention to a particular substrate is to first select the optimum total composition for the coating. This selection is based on the requirements for oxidation resistance and, if required, for a minimum of interaction with the substrate. Each alloy may require a slightly different coating composition to optimize the fulfillment of these requirements; nonetheless excellent service for a number of different alloys may be achieved with a single coating. The degree of optimization that may be performed, principally empirically, before selecting a specific composition will be dictated by the economics of the situation. The total composition is then divided into at least two portions, elements or alloys. This division is based on the consideration of diffusion rates to minimize the required time and/or temperature for the heat treatment. These portions are then produced in powder form and deposited on the substrate. Plasma deposition is essential to this step of the process, because it results in a dense, finely dispersed mixture of the components ideally suited for rapid homogenization and sealing by diffusion. Moreover, a negligible amount of oxidation of the powder particles occurs during the deposition if suitable techniques are employed. Flame-spraying or detonation gun techniques could be employed to deposit the materials in a finely dispersed manner, but are not used in this invention because such techniques are not as desirable as plasma deposition techniques.

When the corrosion resistant coating is intended for wear-resistant application, such as in bearing applications, then wear-resistant hard particles sized between about 0.01 micron and about 10 microns, preferably between about 0.1 and about 1 micron, have to be dispersed throughout the coating. The hard particles, which should be added in sufficient quantity so that they will be substantially uniformly dispersed throughout the coating, should occupy between about 5% and about 75% by volume of the coating composition, preferably between about 10% and 55% by volume. The hard particles are codeposited with the materials of the coating so as to form, after the required heat treatment, a sealed coating having a substantially homogeneous matrix with substantially uniformly dispersed wear-resistant particles, said particles occupying between about 5% and about 75% by volume of the coating and being sized between about 0.01 micron and about 10 microns. In an end use service environment, the coating matrix will wear from friction contact with a mating part and thereby expose a layer of the substantially uniformly dispersed metal particles. The exposed segments of particles on the top of the coated layer will provide good wear-resistant characteristics for the coating and in addition, as such particles wear, new particles will become exposed since according to this invention, particles are substantially uniformly dispersed throughout the coating. The coating of this invention will have, after the heat treatment, a density of greater than about 90% of the theoretical density and essentially zero permeability. Any porosity remaining after the heat treatment will consist, for the most part, of closed pores thus eliminating the inherent interconnected porosity of plasma-sprayed deposits. The particles will be securely embedded in the coating matrix and little or no spalling will occur in wear-resistant applications.

Suitable wear-resistant particles for use in this invention include metal oxides, metal carbides, metal borides, metal nitrides and metal silicides in any combination of mixture thereof. Examples of some metal oxides include such compounds as alumina ( $Al_2O_3$ ), silica ( $SiO_2$ ), chromium sesquioxide ( $Cr_2O_3$ ), hafnium oxide ( $HfO_2$ ), beryllium oxide ( $BeO$ ), zirconium oxide ( $ZrO_2$ ), stannic oxide ( $SnO_2$ ), magnesium oxide ( $MgO$ ), yttrium oxide ( $Y_2O_3$ ), rare earth oxides, and titanium dioxide ( $TiO_2$ ) in any and all mixtures. Suitable metal carbides include silicon carbide ( $SiC$ ), boron carbide ( $B_4C$ ), hafnium carbide ( $HfC$ ), columbium carbide ( $CbC$ ), tantalum carbide ( $TaC$ ), titanium carbide ( $TiC$ ), zirconium carbide ( $ZrC$ ), molybdenum carbide ( $Mo_2C$ ), chromium carbide ( $Cr_3C_2$ ) and tungsten carbide ( $WC$ ). Suitable metal borides include titanium boride ( $TiB_2$ ), zirconium boride ( $ZrB_2$ ), columbium boride ( $CbB_2$ ), molybdenum boride ( $MoB_2$ ), tungsten boride ( $WB_2$ ), tantalum boride ( $TaB_2$ ) and chromium boride ( $CrB$ ). Suitable metal nitrides include aluminum nitride ( $AlN$ ), silicon nitride ( $Si_3N_4$ ), titanium nitride ( $TiN$ ), zirconium nitride ( $ZrN$ ), hafnium nitride ( $HfN$ ), vanadium nitride ( $VN$ ), niobium nitride ( $NbN$ ), tantalum nitride ( $TaN$ ) and

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chromium nitride (CrN). Suitable silicides include molybdenum silicide (MgSi<sub>2</sub>), tantalum silicide (TaSi<sub>2</sub>), tungsten silicide (WSi<sub>2</sub>), titanium silicide (TiSi<sub>2</sub>), zirconium silicide (ZrSi<sub>2</sub>), vanadium silicide (VSi<sub>2</sub>), niobium silicide (NbSi<sub>2</sub>), chromium silicide (CrSi<sub>2</sub>) and boron silicide (B<sub>4</sub>Si<sub>2</sub>).

The following Examples 1 to 6, 8 and 9 illustrate the invention but are not intended to limit it in any way, Example 7 is included for purposes of illustration only.

### EXAMPLE 1

Three nickel-base superalloy (known as 713C—12.5 wt/o Cr, 4.2 wt/o Mo, 2.0 wt/o Nb, 0.8 wt/o Ti, 6.1 wt/o Al, 0.012 wt/o B, 0.01 wt/o Zn, 0.12 wt/o C, remainder Ni) cylindrical pins, measuring 1/4 inch diameter by 3 inches long, were each given a plasma-deposited coating of one of the coating compositions shown in Table 1. The coating composition was a mixture of pure aluminum powder with an alloy of nickel-chromium powder (Ni—20 wt/o Cr) sized 325 Tyler mesh and finer. The proportions of the aluminum to the alloy are shown in Table 1.

TABLE 1		
Coating	Wt/o Al	Wt/o Ni—Cr Alloy
A	20	80
B	30	70
C	40	60

Each of the mixed powders was plasma-deposited on the circumference of one of the pins for a length of 2 1/2 inches and for a thickness of 0.004 inch. The coated pins were then heat treated in a hydrogen atmosphere at 1100°C for 6 hours after which they cooled to ambient temperature. A metallographic examination of pieces cut from the heat treated coated pins showed that coating A had formed a solid coating, with an essentially two-phase structure; predominantly  $\beta$ , Ni(Cr)Al, with a network of  $\gamma'$  Ni(Cr)<sub>2</sub>Al<sub>3</sub>.  $\beta$  and  $\gamma'$  are crystalline structures wherein Cr is substituted for some of the Ni in the crystalline lattice of the intermetallic compound. Some Cr was dissolved in each of the above phases and a portion precipitated on cooling as  $\alpha$  (Cr solid solution). Cr solid solution exists when a solid Cr matrix has dispersed throughout it, in a random manner, other elements. There was a negligible amount of interaction with the substrate. Coating B was also a solid coating, but was virtually solid  $\beta$  phase with a dispersion of  $\alpha$  formed on cooling. However some interaction with the substrate had occurred, forming a multiple phase columnar zone at the substrate surface. Coating C was similar to coating B but the columnar zone was wider and a new zone of pure  $\beta$  had grown between the substrate and the original coating as a result of the diffusion of Ni out-

ward and Al inward. In all three coatings virtually all the porosity was eliminated. All three coatings were oxidized at 1200°C for 100 hours in dry air. All three formed a protective exterior scale of what appeared to be almost pure Al<sub>2</sub>O<sub>3</sub>. Although part of the  $\beta$  phase was converted to  $\gamma'$  or  $\gamma$  (Ni solid solution) as a result of the diffusion of Al to the surface followed by its oxidation, the total thickness of the coating was not significantly reduced.

### EXAMPLE 2

A nickel-base superalloy (20 wt/o Cr, 13 wt/o Mo, 0.45 wt/o Mn, 0.3 wt/o Si, 0.1 wt/o La, remainder Ni) cylindrical pin, measuring the same as in Example 1, was plasma sprayed with a mixture of aluminum powder and Ni—Cr alloy powder (Ni—20 wt/o Cr). The mixture contained 10 wt/o pure Al with the remainder Ni—Cr, and was sized 325 Tyler mesh and finer. After a thickness of 0.003 inch was deposited, the coated pin was heat treated in a vacuum for 4 1/2 hours at 1079°C. The heat treated coated pin was then subjected to a cyclic oxidation test whereupon it was heated for 2 1/2 hours in a furnace at 1150°C followed by exposure to ambient temperature for 1/2 hour. After being cyclically oxidized for 120 hours, the coated pin was statically oxidized for another 120 hours at 1150°C. A metallograph examination revealed that although the aluminum concentration was too low to form much  $\beta$  phase during the heat treatment, the coating was completely sealed and formed what appeared to be a pure Al<sub>2</sub>O<sub>3</sub> scale during oxidation which prevented any detected loss in coating thickness.

### EXAMPLE 3

A nickel base superalloy (known as B1900—8.0 wt/o Cr, 10.0 wt/o Co, 6.0 wt/o Mo, 1.0 wt/o Ti, 6.0 wt/o Al, 0.015 wt/o B, 0.10 wt/o Zr, 4.0 wt/o Ta, 0.10 wt/o C, remainder Ni) cylindrical pin, measuring the same as in Example 1, was plasma sprayed with a mixture of powders as in Example 2. After a coating thickness of 0.005 inch was deposited, the pin was heat treated at 1100°C for 4 hours in argon. The heat treated coated pin was then subjected to a cyclic oxidation test as in Example 2 for 120 hours at 1095 to 1135°C followed by another 102 hours at 1150°C in air. A metallographic examination revealed that the coating was completely sealed and a continuous protective scale of Al<sub>2</sub>O<sub>3</sub> formed on the surface. No detectable loss in coating thickness was noted.

### EXAMPLE 4

A nickel base superalloy (known as B1900 and defined in Example 3) cylindrical pin, measuring the same as in Example 1, was



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plasma sprayed with a ternary mixture of elemental powders, sized 325 Tyler mesh and finer, consisting of 22 wt/o Cr, 17 wt/o Al, and 61 wt/o Ni. After a coating thickness of 0.003 inch was deposited, the pin was heat treated at 1100°C for 4 hours in argon. The heat treated pin was then subjected to a cyclic oxidation test as in Example 2 for 120 hours at 1095 to 1135°C, followed by another 102 hours at 1150°C in air. A metallographic examination revealed that the coating was completely sealed and a continuous protective scale of  $Al_2O_3$  formed on the surface. No detectable loss in coating thickness was noted.

#### EXAMPLE 5

A nickel base superalloy (known as B1900 and defined in Example 3) cylindrical pin, measuring the same as in Example 1, was plasma sprayed with a mixture of powders, sized 325 Tyler mesh and finer, consisting of 10 wt/o pure aluminum and 90 wt/o of an alloy of Fe-25Cr-13Al-1Y (wt/o). After a coating thickness of 0.002 inch was deposited, the coated pin was heat treated at 1100°C for 4 hours in argon. This produced a three-layer coating with an outer zone of Fe-Ni-Cr solid solution, a center band of  $\beta$ , and a columnar zone beneath the original pin surface. This structure was due, for the most part, to the diffusion of Ni from the substrate outward. The coating exhibited a rough exterior surface because of the spraying conditions, and after the heat treatment, there was a small amount of porosity in the outermost region which was somewhat oxidized due to impure argon during the heat treatment. However, with the exception of this small fraction of oxidized area of the total coating, a solid structure was obtained that provided adequate oxidation protection during the same oxidation exposure as given in Example 3. In fact, a broader band of  $\beta$  remained after oxidation.

#### EXAMPLE 6

A nickel base superalloy (defined in Example 2) cylindrical pin, measuring the same as in Example 1, was plasma sprayed with a mixture of four powders, Fe+12Al+25Cr+0.45Y $_2$ O $_3$  (wt/o), sized 325 Tyler mesh and finer. After a coating thickness of 0.003 inch was deposited, the coated pin was heat treated for 164 hours at 1079°C in H $_2$  to form a sealed coating. The pin was then oversprayed with a plasma deposit of pure Al to a thickness of 0.0015 inch. The pin was again heat treated for 64 hours at 1080°C in H $_2$ . The resulting microstructure had three zones similar to that in Example 5 with no porosity. One segment of the coated pin was subjected to a cyclic oxidation test at 1150°C as in Example 2, and resulted in a continuous protective scale of  $Al_2O_3$ ,

being formed on the surface. No detectable loss in total coating thickness was noted although some of the phase had converted to  $\beta$  or  $\gamma'$  due to the depletion of Al by diffusion to the scale. A second segment of the coated pin was cyclically oxidized at 1200°C for 120 hours and remained virtually constant in total thickness even though most of the Al in the coating was consumed.

#### EXAMPLE 7

A similar coating to that of Example 6 was produced except that the additional aluminum was added by a conventional pack cementation process. The heat treated coated pin was subjected to the same cyclic oxidation test as in Example 6 at a temperature of 1150°C. A metallographic examination revealed that the coating thickness was substantially unchanged but was somewhat more degraded than the coated pin in Example 6 because less aluminum was added by the pack cementation process.

#### EXAMPLE 8

A bar of nickel base superalloy (known as B1900 and defined in Example 3), having a cross-sectional shape of a gas turbine blade and measuring 3 inches overall length, cut into segments varying from 3/8 to 1/2 inch long, was plasma sprayed with a mixture of 80 wt/o of an alloy powder of Co-Cr-Y and 20 wt/o of pure aluminum powder, sized 325 Tyler mesh and finer. The alloy was composed of 79 wt/o Co, 20 wt/o Cr, and 1 wt/o Y. After a coating thickness of 0.005 inch was deposited, the coated bar was placed in an  $Al_2O_3$  boat and heat treated for 5 hours at 1100°C in 5 cfm argon in a 2-inch-diameter furnace. The heat treated coated bar was then cyclically oxidized in dry air for 120 hours at 1150°C. No significant spalling was observed and only minor internal oxidation of the coating was noted.

#### EXAMPLE 9

Several sets of experiments were run to determine the utility of using a coating sealed by the reaction/diffusion of two metallic components, but also incorporating a dispersion of hard particles to increase the wear resistance of the coating. First, the series of coatings shown in Table 2 were tested for oxidation resistance. All of the coatings were 0.0050 to 0.0055 inch thick and applied by plasma deposition to 3-inch-long by 1/4-inch-diameter pins of a nickel base superalloy known as 713C over a length of 24 inches. They were then cut into 1/4-inch-long segments. The first three coatings A through C were sealed by heat treatment in a hydrogen atmosphere for 4 hours at 900°C according to this invention. The other coatings D through G represent typical oxidation resistant matrices with hard particle dispersions, but are not

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capable of being sealed by a heat treatment process.

- 5 The oxidation test consisted by cycling between 1000°C and approximately ambient temperature for a total of 120 hours. The specimens were held at 1000°C for 2½ hours and at ambient temperature for ½ hour in each cycle. After testing, the cross sections of the specimens were examined metallographically with the results shown in Table 2. It is evident that the first two sealed coatings (A

and B) were superior to the rest. The third sealed coating (C) was better than the rest, but still unsatisfactory, since it was cracked. Thus it can be concluded that the volume fraction of oxide was too high to allow effective sealing and/or resist thermal shock. The conventional coatings probably failed because the substrate was oxidized through the porosity of the coating. Thus the coating/substrate interface was weakened and could not withstand the thermal shock.

TABLE 2

Coating Composition, wt/o	Al <sub>2</sub> O <sub>3</sub> vol/o	Oxidation Results
A—82.6 NiCr+9.2 Al+ 8.2 Al <sub>2</sub> O <sub>3</sub>	15	no degradation
B—59.7 NiCr+6.6 Al+37.7 Al <sub>2</sub> O <sub>3</sub>	50	no degradation
C—23.2 NiCr+2.6 Al+74.2 Al <sub>2</sub> O <sub>3</sub>	85	coating cracked
D—26.7 Hastelloy X +73.3 Al <sub>2</sub> O <sub>3</sub>	85	completely spalled
E—92.2 Hastelloy X + 7.8 Al <sub>2</sub> O <sub>3</sub>	15	excessive spalling
F—27.9 Stellite 31 +72.1 Al <sub>2</sub> O <sub>3</sub>	85	excessive spalling
G— 9 Cobalt +91 WC		coating oxidized

- 35 Stellite is a Registered Trade Mark. NiCr alloy is 80 wt/o nickel and 20 wt/o chromium. The Al<sub>2</sub>O<sub>3</sub> 1 micron alumina known as Linde C and obtainable from Union Carbide Corporation. (Linde is a Registered Trade Mark). The WC—Co coating is known as UCC plasma-deposited coating LW—10. The Hastelloy X alloy is a trade name of Cabot Corporation for a powder composition of 22Cr, 0.6W, 9.0Fe, 0.02C, 0.5Si, 0.015Co, 0.5Mn, 9.00Mo, 0.02P, 0.015S and remainder Ni (wt/o). Stellite 31 is a Trade Mark of Cabot Corporation for a powder composition of 25.5Cr, 7.5W, 1.0Fe, 0.5C, 0.5Si, 10.5Ni, 0.5Mn, 0.02P, 0.02S and remainder Co (wt/o).

- 50 A second series of experiments was designed to test the applicability of this type of coating on steel substrates. In the first experiment, a 1-inch-wide by 1-inch-OD 304 stainless steel ring with 1/8-inch-thick wall was coated with a mixture of 53 wt/o of an alloy of Fe—Cr (80 wt/o Fe and 20 wt/o chromium), 9.5 wt/o unalloyed Al and 37.5 wt/o (50 vol/o) Al<sub>2</sub>O<sub>3</sub> (1 micron Linde C alumina) to a thickness of 0.007 inch. The ring was heat treated for 12 hours in hydrogen at 900°C to seal the matrix by reaction/diffusion. It was then cyclically oxidized for 120 hours between 900°C and about room temperature. Each cycle consisted of 2½ hours at 900°C and ½ hour at room temperature. No degradation was observed visually or metallographically. In a second experiment similar results were obtained with a mixture of 59.8 wt/o of a Ni—Cr alloy (80 wt/o Ni and 20 wt/o Cr), 6.5 wt/o unalloyed Al and 33.7 wt/o (50 vol/o) Al<sub>2</sub>O<sub>3</sub> (1 micron Linde C alumina). It was plasma-deposited

as a 0.0065-inch-thick coating on a 1-inch-diameter by 1-inch-high solid cylinder of 1018 steel. After sealing by heat treating at 700°C for 12 hours in hydrogen, it was cyclically oxidized as above. Only minor cracking was observed metallographically.

In another series of experiments, a series of conventional coatings and alloys was compared with a sealed NiCr—Al—Al<sub>2</sub>O<sub>3</sub> produced according to the concepts presented here in a self-mating, high-temperature wear test. The materials tested and the results are shown in Table 3. The sealed coating of this invention was prepared by plasma depositing a mixture of 59.7 wt/o of NiCr alloy (80 wt/o Ni and 20 wt/o Cr), 6.6 wt/o Al, and 33.7 wt/o Al<sub>2</sub>O<sub>3</sub> (1 micron Linde C alumina) on Hastelloy X wear test mating surfaces, such surfaces being the end faces of different size cylindrical members. One of the cylindrical members was rotated while contacting the other member so that the friction interaction between the coated end faces will provide a depression or scar volume indicative of wear. The coatings were sealed by heat treating at 1079°C for 4 hours in argon. The Hastelloy X specimens were uncoated. The plasma-deposited Hastelloy X contained 7.8 wt/o Al<sub>2</sub>O<sub>3</sub> (1 micron Linde C alumina). The LW—10 is a commercial plasma-deposited mixture of 9 wt/o cobalt and 91 wt/o WC. One of the wear test surfaces was rotated at a speed of 45 rpm (relative speed between surfaces of 53.3 ft/min) at a temperature of 650°C for a period of 7 hours under loads of 100, 300, and 500 psi. It is evident that the coating of this invention gave superior wear resistance and oxidation resistance.



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TABLE 3

	Coating	Load (psi)	Scar Vol, 10 <sup>-4</sup> in. <sup>2</sup>
5	A—NiCr+Al+Al <sub>2</sub> O <sub>3</sub>	100	0 (not measurable)
		300	0 (not measurable)
		500	741.
	B—Plasma Hastelloy X+Al <sub>2</sub> O <sub>3</sub>	100	40.1
		300	651.
		500	too high to complete test
10	C—Wrought Hastelloy X	100	29.2
		300	252.
		500	3363.
	D—Wrought Inconel X	100	24.4
		300	638.
		500	4590.
15	E—IW—10	100	791
		300	740
		500	728

Inconel is a Registered Trade Mark.

20 Attention is directed to our copending application No. 24046/73 which claims:

1. A process for producing a corrosion resistant duplex coated article comprising:

25 a) depositing by plasma deposition techniques an undercoat layer comprising an intimate mixture of at least two materials, each of which is selected from metal, alloys, and intermetallics, onto an article such that the materials are deposited in a substantially unreacted state;

30 b) heating said coated article in a non-oxidising atmosphere at a temperature and for a time period sufficient to cause the intermetallics, metal oxides, metal carbides, metal nitrides, metal borides, metal silicides, and cermets, onto the as-deposited undercoat; and

35 c) heating said duplex coated articles in a non-oxidising atmosphere at a temperature and for a time period sufficient to cause the substantially unreacted materials in the undercoat layer to react/diffuse together without significant reaction with the underlying article thereby forming a substantially sealed undercoat layer.

40 2. A process for producing a corrosion resistant duplex coated article comprising:

45 a) depositing by plasma deposition techniques an undercoat layer comprising an intimate mixture of at least two materials, each of which is selected from metals, alloys, and intermetallics, onto an article such that the materials are deposited in a substantially unreacted state;

50 b) heating said coated article in a non-oxidising atmosphere at a temperature and for a time period sufficient to cause the substantially unreacted materials in the undercoat layer to react/diffuse together without significant reaction with the underlying article thereby forming a substantially sealed undercoat layer; and

55 c) depositing a primary coating selected from at least one of:

metals, metal alloys, intermetallics, metal oxides, metal carbides, metal nitrides, metal borides, metal silicides, and cermets, onto the substantially sealed undercoat layer thereby producing a duplex layer having excellent corrosion-resistant characteristics.

However, we make no claim herein to either of these processes.

Subject to the foregoing disclaimer,

WHAT WE CLAIM IS:—

1. A process for producing a corrosion resistant coated article comprising:

75 a) depositing by plasma deposition techniques a coating of an intimate mixture of at least two materials, each of which is selected from metals, alloys, and intermetallics, onto an article such that the materials are deposited in a substantially unreacted state; and

80 b) heating said coated article in a non-oxidising atmosphere at a temperature and for a time period sufficient to cause the substantially unreacted materials in the coated layer to react/diffuse together without substantial reaction with the underlying article thereby forming a substantially sealed corrosion resistant layer.

2. The process claimed in claim 1 wherein the metals are selected from nickel, aluminum, cobalt, iron, chromium, copper, molybdenum, tungsten, niobium, tantalum, zirconium, vanadium, hafnium, titanium, zinc and manganese; wherein the alloys are selected from the alloys of the above metals, and wherein the intermetallics are selected from the intermetallics of the above metals.

3. The process claimed in claim 1 wherein each of the materials in step a) is selected from nickel, aluminum, cobalt, iron, chromium, copper, molybdenum, tungsten, niobium, tantalum, titanium, zirconium, vanadium, hafnium, zinc, manganese, nichrome, silicon,

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iron-chromium alloys, iron-chromium intermetallics, cobalt-chromium alloys, cobalt-chromium intermetallics, nickel-chromium-silicon alloys, nickel-chromium-silicon intermetallics, cobalt-chromium alloys, cobalt-cobalt-chromium-silicon intermetallics, iron-chromium-silicon alloys, iron-chromium-silicon intermetallics, iron-chromium alloys containing rare earth additions, nickel-chromium alloys containing rare earth additions, cobalt-chromium alloys containing rare earth additions, copper-aluminum alloys and copper-aluminum intermetallics.

4. The process claimed in claim 3 wherein the material of the article is selected from the base alloys of Re, Ni, and Co; and wherein in step a) one of the materials is aluminum and the other material is selected from iron-chromium alloys, nickel-chromium alloys and cobalt-chromium alloys;

5. The process claimed in claim 1 wherein an additional step is added after step b) as follows:

c) subjecting the coated article to an atmosphere selected from an oxidizing atmosphere, a carburizing atmosphere, a nitriding atmosphere, a boriding atmosphere, and a siliciding atmosphere for a time period and at a temperature sufficient to react the medium in the atmosphere with the surface of the coated layer thereby providing a surface layer of the reacted medium on said coated article.

6. The process claimed in claim 4 wherein after step b) the following step is added:

c) subjecting the coated article to an oxidizing environment for a time period and at a temperature sufficient to oxidize the surface of the coated layer thereby providing an oxidized layer on said coated article.

7. The process claimed in claim 5 wherein the medium in the environment is present in a sufficient amount and under a partial pressure so as to effectively react the medium with one of the elements on the surface layer of the coated article.

8. The process claimed in claim 4 wherein

the aluminum proportion is present in an amount between 8 wt/o and about 25 wt/o the total coating composition, and the chromium proportion is present in an amount between about 10 wt/o and about 25 wt/o the total coating composition.

9. The process claimed in claim 8 wherein a rare earth element is present in an amount between about 0.01 wt/o and about 5 wt/o the total coating composition.

10. The process claimed in claim 8 wherein silicon is present in an amount between about 0.1 wt/o and about 5 wt/o the total composition.

11. The process claimed in claim 3 wherein the material of the article is selected from Cr, Nb, Ta and Mo; and wherein in step a) one of the materials is silicon and the other material is selected from niobium, tungsten, chromium, titanium, vanadium, aluminum, boron, iron and manganese.

12. The process claimed in claim 3 wherein the material of the article is copper base alloy and wherein in step a) the materials are aluminum and a copper base alloy.

13. The process claimed in claim 3 wherein particles are plasma deposited along with the coating materials, said particles being sized between about 0.01 micron and about 50 microns; present in sufficient quantity to occupy between about 1% and about 75% of the volume of the coating; and selected from metal oxides, metal carbides, metal borides, metal nitrides, and metal silicides.

14. A process as claimed in claim 1 and substantially as hereinbefore described with reference to the Examples.

15. Coated articles, whenever produced by the process claimed in any one of claims 1 to 14.

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